PB86-119096

Effect of Dissolved Solids on Limestone FGD (Flue Gas Desulfurization) Scrubbing Chemistry

Peabody Process Systems, Inc., Stamford, CT

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Oct 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-119096

EPA/600/D-85/266
October 1985

THE EFFECT OF DISSOLVED SOLIDS ON LIMESTONE FGD SCRUBBING CHEMISTRY

by

Dennis Laslo
Even Bakke

Peabody Process Systems
Stamford, CT 06907

Revokable License Agreement 06-043-81

EPA Project Officer
J. David Mobley

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/D-85/266	2.
3. RECIPIENT'S ACCESSION NO. PB86 119096/AS	
4. TITLE AND SUBTITLE The Effect of Dissolved Solids on Limestone FGD Scrubbing Chemistry	5. REPORT DATE October 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Dennis Laslo and Even Bakke	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Peabody Process Systems, Inc. 835 Hope Street Stamford, Connecticut 06907	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. Revokable License Agreement 06-043-81
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Published paper; 3/83
	14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES J. David Mobley is the IERL-RTP project officer: Mail Drop 61, 919/541-2578.

16. ABSTRACT

The paper gives results of experiments in a 0.1 MW pilot plant to determine the effects of high concentrations of chloride ions and dissolved salts on flue gas desulfurization (FGD) scrubbing chemistry, both in the natural and forced oxidation modes of operation. (Note: The tightly closed water loops in FGD systems promote the buildup of soluble salts in the recirculating scrubbing liquor.) As the concentration of calcium chloride increased, significant decreases in sulfur dioxide (SO_2) removal efficiency were measured. The decreases are shown to be independent of absorber inlet SO_2 concentration and liquid/gas ratio, but not independent of degree of oxidation and excess limestone in the slurry. A semi-empirical model, that explains both natural and forced oxidation SO_2 removal data, was developed. An overview of the problem and a summary of test results to date are given in detail.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B 07
Desulfurization	Stationary Sources	07A, 07D 12A
Flue Gases	Dissolved Solids	21B
Scrubbers		13I
Dissolving		
Calcium Chlorides		07B
Chemistry		
Mathematical Models		

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 26
	20. SECURITY CLASS (This page) Unclassified	22. PRICE $9.95

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

1.0 ABSTRACT

The advent of tightly closed water loops in flue gas desulfurization (FGD) systems promotes the buildup of soluble salts in the recirculating scrubbing liquor.

Experiments were conducted in a 0.1 MW pilot plant to determine the effects of high concentrations of chloride ions and dissolved salts on FGD chemistry, both in the natural and forced oxidation modes of operation. As the concentration of calcium chloride increased, significant decreases in SO_2 removal efficiency were measured. The decreases are shown to be independent of absorber inlet SO_2 concentration and liquid to gas ratio but not independent of degree of oxidation and excess limestone in the slurry.

A semi-empirical model, which explains both natural and forced oxidation SO_2 removal data, was developed.

An overview of the problem and a summary of test results to date are given in detail.

Although the research described in this paper has been funded in part by the U.S. Environmental Protection Agency and although it has been subjected to review by the Agency, it does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

2.0 NOMENCLATURE

C	Component concentration
G	Gas flow rate
H	Henry's Law constant
K	Solubility product
$K_g a$	Overall mass transfer coefficient
L	Liquid flow rate
N	Molar flux
P	Component partial pressure
R	Ratio constant defined by Eq. (6)
a	Total mass transfer surface area
k_g	Gas-side mass transfer coefficient
f	Fraction SO_2 removal
ℓ	Total height of the absorbing section
ϕ	Mass transfer enhancement factor (dimensionless)

Subscripts:

b	Base case test
i	Gas/liquid interface
t	Total
x	Tests run at high concentrations of dissolved salts

Superscripts:

o	Bulk liquid
$*$	Gas/liquid interface

3.0 BACKGROUND

Material balance calculations have shown that, for most flue gas desulfurization (FGD) systems with a potential for operation at high dissolved solids, the primary source of these solids will be from the absorption of the HCl gas formed during combustion by chlorides in the coal. Most HCl in the flue gas is absorbed into the FGD system, reacts with the alkaline reagent (usually lime or limestone), and concentrates as the salt, calcium chloride.

In addition, conservation of water usage in the generation of electrical power has been achieved by the use of cooling tower blowdown (CTB) as makeup water to FGD systems. Soluble salts, such as sodium chloride and sodium sulfate in the CTB water, concentrate in the FGD system and further increase the steady state dissolved solids in the scrubber loop.

If closed-loop operation is assumed (i.e., the only water leaving the FGD system is through evaporation and filter cake moisture), material balance calculations, for high chloride coals, indicate that dissolved solids can accumulate to levels exceeding 5 weight percent (Ref. 1,2,3). Forced oxidation intensifies the accumulation through improved cake dewatering, and dissolved solids can reach worst case levels in excess of 15 weight percent (Ref. 1,2,3).

It is possible to reduce dissolved solids in the FGD system by several different methods. A prescrubber would concentrate chlorides and reduce TDS levels in the FGD system but would require a purge stream, or open loop operation. A purge of FGD liquor, also open-loop operation, would eliminate the cost of a prescrubber but, comparing this method to a prescrubber, higher TDS levels would result in the FGD system. Concentrating and then removing the dissolved salts has been suggested by using vapor-compression evaporaters (Ref. 4) or spray dryers (Ref. 5) but have not been commercially tested. Ocean disposal may be an option as well as fixation and landfill disposal of a purge stream (Ref. 6), but both present permitting uncertainties.

Allowing the dissolved salts to accumulate to equilibrium in the FGD liquor is the most economical solution if suitable alloys or linings are used to prevent corrosion and there are no detrimental effects to the FGD process chemistry. The test work described in this paper was undertaken in an attempt to characterize SO_2 absorption, using lime or limestone scrubbing, in the presence of high concentrations of dissolved solids.

4.0 LITERATURE REVIEW

A literature review on previous work in this area as well as interim results on this testwork were presented at the EPA/EPRI FGD symposium in Hollywood, FL (Ref. 1). As reported, test results in the 0.1 MW EPA mobile bed pilot plant indicated that, as chloride concentrations in the scrubbing liquor increased, a significant decrease occurs in the SO_2 removal efficiency. As shown in Figure 1, at constant absorber parameters, removal efficiencies declined for both the natural and forced oxidation modes of operation. Also, as chloride concentrations increased, the scrubbing liquor pH decreased as shown in Figure 2. In an attempt to overcome the decrease in removal efficiencies, excess limestone was added until the efficiency was equal to the base case efficiency (the base case is the test run with no chlorides in the scrubbing liquor). Figure 3 summarizes the results of these experiments, indicating the quantity of excess limestone required is unacceptable for high chloride concentrations. Also, an organic acid additive, dibasic acid (DBA), was tested as a means of overcoming the effects of chlorides. Figure 4 indicates that only 9 meq/l (650 PPM) of DBA was required to restore the SO_2 removal efficiency at a concentration of 50,000 mg/l of chloride ions.

Recently, extensive research and development efforts have been undertaken in the area of the effects of dissolved solids on lime/limestone FGD systems:

1) EPRI contracted Radian Corporation to examine the effects of TDS on SO_2 mass transfer in a bench top absorber. Included in this work was a simulation of the Peabody/EPA pilot plant work for natural and forced oxidation.

2) Peabody and EPA entered into a cost sharing agreement to continue the pilot plant program for the investigation of producing commercial grade gypsum in the presence of high TDS, examining the effectiveness of organic acid additives at high TDS, testing cations other than Ca^{++}, and using lime instead of limestone as the alkali.

3) Professor Gary Rochelle at the University of Texas has initiated research in the theoretical modeling of gas/liquid mass transfer, $CaSO_3$ dissolution, and $CaCO_3$ dissolution in the presence of high concentrations of dissolved solids.

4) EPRI, TVA, and Babcock and Wilcox have studied chloride ion effects in the 10MW spray tower at TVA's Shawnee test facility. Results have not been published as of this writing.

Combustion Engineering (CE) conducted pilot plant tests on a 1200 ACFM pilot plant on two occasions. Initially, Rader (Ref. 7) reported an increase in SO_2 removal efficiencies as chloride ion concentrations increased. In a subsequent report (Ref. 8), CE tests indicated no effect of chloride ions on SO_2 removal efficiencies with inlet flue gas SO_2 concentrations ranging from 500 to 1500 PPM and chloride ion concentrations as high as 80,000 mg/liter. Although seemingly contradictory, the first tests were run at constant pH and the second set of tests were run at a constant limestone stoichiometry. The tests certainly contradicted results obtained by Peabody (Ref. 1) in a mobile bed pilot plant. Rader attributed the differences in results to the high liquid holdup of the mobile bed absorber and relatively high inlet SO_2 concentration of 2500 PPM utilized in the Peabody/EPA tests.

5.0 THEORY

As mentioned previously, there are primarily two sources of dissolved species in FGD slurry; HCl gas absorption, and dissolved salts in the makeup water. Absorption of HCl in the FGD scrubber will result in a corresponding increase in the concentration of calcium ions when lime or limestone are used as the alkali:

$$HCl_{(g)} + H_2O \rightleftharpoons H^+ + Cl^- + H_2O$$

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{++} + CO_2 + H_2O$$

Ions entering the system from the makeup water quickly reach solid/liquid equilibrium and concentrate due to scrubber evaporative losses.

As reported by Chang and Laslo (Ref. 1) the equilibrium pH is a function of the calcium ion concentration:

$$C_{H^+} = K \, (C_{Ca^{++}})^2 \cdot P_{CO_2}$$

The molar flux of SO_2 into the absorbing slurry, by material balance, must be the same in the gas and liquid film and is expressed as,

$$N_{SO_2} = k_1^o \, \phi \, (C_{SO_2}^* - C_{SO_2}) = k_g \, (P_{SO_2} - P_{SO_2}^i) \qquad (1)$$

The rate of SO_2 absorption in the absorber can be written for a differential height as follows,

$$\frac{-G \, dSO_2}{P_t dz} = K_g a \, (P_{SO_2} - P_{SO_2}^i) \qquad (2)$$

where,

$$K_g a = \left(\frac{1}{k_g a} + \frac{H}{\phi k_1^o} \right)^{-1} \qquad (3)$$

Wang and Burbank (Ref. 9) simplified equations (2) and (3) for limestone scrubbing since $P_{SO_2}^i \ll P_{SO_2}$ and the liquid-side resistance is dominant (i.e., $\frac{k_1^o \phi}{H} \ll k_g$), which after integration, yielded,

$$f = 1.0 - EXP \, (- \phi \, k_1^o \, a \, z / H \, G) \qquad (4)$$

or, taking the log of both sides,

$$\ln (1.0 - f) = -\phi k_l^o a z / H G \qquad (5)$$

The enhancement factor, ϕ , is strongly affected by solution equilibria. A high concentration of bisulfite ions, which occurs at a low pH, depresses the hydrolysis of SO_2 and reduces mass transfer. Additives such as adipic acid or magnesium oxide increase ϕ as would the presence of an oxidation catalyst such as manganese.

Referring to equation (5), the parameters G, K, a, and z will be affected by absorber related variables such as sphere static bed height, slurry flow rate, and gas flow. Henry's Law constant, H, is not expected to change significantly as the concentration of dissolved solids increases (Ref. 1).

In order to compare the effect of total dissolved solids on SO_2 mass transfer and minimize the effects of scrubber variables (such as the liquid to gas ratio), the ratio of equation (5) with dissolved solids to equation (5) without dissolved solids (labeled the base case), provides the following,

$$R = [\ln (1.0 - f)]_x / [\ln (1.0 - f)]_b \qquad (6)$$

If K , z , H , and G remain constant, R gives an indication of the change in the enhancement factor ϕ .

6.0 TEST FACILITIES

Peabody Process Systems and the U.S. Environmental Protection Agency signed an innovative agreement which allowed Peabody to use government owned equipment in a government facility. The equipment involved is EPA's in-house,0.1 MW limestone FGD pilot plant and associated analytical laboratories located at the Industrial Environmental Research Laboratory in Research Triangle Park, North Carolina. Acurex Corporation was contracted to operate and maintain both the pilot plant equipment and the laboratories.

Two process configurations, natural and forced oxidation, shown in Figures 5 and 6, were employed for the tests. The absorber is a three stage turbulent contact absorber (TCA), with a capacity of 7.5 cu. m/min of flue gas. No flyash is present as the gas is drawn from a natural gas fired boiler and injected with pure SO_2 as required. The oxidizer is a 30 cm. diameter tower containing slurry at a depth of 5.5 m and was sparged with air from the tower bottom. A bleed stream of the slurry from the hold tank was directed to the clarifier and then processed by a rotary drum vacuum filter to remove the precipitated waste. All filtrate was returned to the scrubber in order to maintain closed loop operation. The system was manually controlled in a feed forward mode by maintaining a constant limestone stoichiometric ratio of moles of reagent added per mole of SO_2 absorbed. A small amount of limestone was also added to neutralize absorbed HCl gas during some tests.

The gas phase SO_2 concentration was monitored continuously using a DuPont 400 SO_2 analyzer and occasionally checked by wet gas titration. Liquid and solid samples of important species such as calcium, sulfite, sulfate, carbonate, magnesium, and sodium were analyzed.

7.0 RESULTS AND DISCUSSION

All tests were run by first establishing baseline scrubber performance without dissolved solids. Then, as dissolved solids were added, all system parameters were held constant. One exception was the limestone feed rate. If the SO_2 removal efficiency decreased, the limestone feed rate was lowered in order to keep the excess limestone in the absorber constant. Of course, when SO_2 removal efficiencies decrease, the waste stream flow rate decreases thereby increasing the system solids residence time. This may alter the calcium sulfite crystal size and thereby alter the calcium sulfite dissolution in the absorber or have an effect on the solids settling rate.

Tests were first run using calcium chloride as the dissolved species, both in the natural and forced oxidation modes. Tables 1 and 2 summarize the results of these tests at various ionic strengths as compared to the base case.

As is evident in both tables, the effect of the chloride ion is to produce a significant decrease in the SO_2 removal efficiency, a predictable decrease in pH, a decrease in solids settling rate, and an increase in gypsum saturation levels. These results were covered briefly in the literature review and in detail by Chang and Laslo (Ref. 1)

In addition to these tests, a series of tests was run at a lower limestone stoichiometry with a very high and very low base case SO_2 removal efficiency, or high and low make-per-pass (make-per-pass is the amount of SO_2 absorbed per unit volume of scrubbing liquid). In addition, two levels of inlet SO_2 concentration were tested, 500 and 2500 PPM. The purpose of these tests was to broaden the original data base by including potential effects of liquid holdup in the absorber, SO_2 make-per-pass, and the inlet SO_2 concentration which affects the gas-side to liquid- side mass transfer resistance ratio. In addition, tests were run at high concentrations of chlorides to determine the amount of excess limestone addition required to restore the original base case efficiency.

Results are presented in Table 3 for the low make-per-pass tests (which were run with no packing in an open spray tower), and Table 4 for the high make-per-pass tests (run with the maximum possible packing height).

Since it is difficult to compare tests at different base case conditions, R from Equation (6) was calculated for each test. Figure 7 summarizes the natural and forced oxidation values for R plotted as a function of the chloride ion concentration. It is apparent that R has a linear correlation with the chloride concentration and is independent of inlet SO_2 concentration, make-per-pass, liquid holdup in the absorber, and the liquid to gas ratio. This suggests that R is directly correlated with $\emptyset$, and the primary effect of chlorides on SO_2 removal is due to changes in gas/solid/liquid equilibria. This contradicts results reported by Rader (Ref. 8), although possibly the CE tests were run at high flue gas oxygen levels. High oxidation rates would negate the mass transfer slowdown through the oxidation of the bisulfite ion. Figure 7 also indicates that the intial base case pH is significant as is the degree of oxidation. Tests run with an initial pH of 6.0 (or a limestone stoichimetry of 1.3-1.4) have a slope significantly steeper than the tests run with an initial pH of 5.8-5.9 (or a limestone stoichimetry of 1.15-1.20). Possibly some limestone blinding occurred during the tests with higher limestone stoichiometries (and higher base case pH). Note that the forced oxidation process is not affected by chlorides as severely as the natural oxidation process. This may be due to the lower

bisulfite concentration at the scrubber inlet and lack of calcium sulfite dissolution in the absorber.

Tests were run to determine the amount of excess limestone that was required to restore the base case SO_2 removal efficiency. As can be seen in Table 3, for runs LM-2 and LM-4, limestone utilizations of 0.48-0.52 (stoichiometric ratio of 1.9-2.0) are required to restore the base case efficiency at both high and low inlet SO_2 concentrations. In Table 4, runs HM-2 and HM-4, limestone utilizations of 0.43-0.63 (stoichiometric ratio of 1.6-2.3) were required during the high make-per-pass runs. These tests were short in duration, and the limestone addition was by manual control. Although there is scatter in the data, the values seem to indicate the amount of excess limestone required to restore the SO_2 removal efficiency is independent of inlet SO_2 concentration and make-per-pass. However, referring to Figure 3, during natural oxidation runs with a higher base case pH, the limestone stoichiometry required to restore base case efficiency at 50,000 mg/l of chlorides, would be nearly 4.0 (utilization of 0.25). Again, there may have been limestone blinding occurring during the tests with the higher base case pH.

In addition to tests performed using calcium chloride as the dissolved salt, tests were run with a mixture of sodium chloride and calcium chloride. Results are presented in Table 5. The tests were run such that in test NN-1, only NaCl was added. In test NN-2, approximately 50 percent of the chloride was as NaCl and the remainder as calcium chloride. In NN-1, no effect on removal efficiency was observed. Test NN-2 did show a drop in removal efficiency and pH similar to tests without sodium but at a chloride concentration of 25,000 mg/l rather than the actual 50,000 mg/l. Apparently sodium has no effect and only the calcium concentration is important. The calculated R values also correspond to concentrations of calcium chloride. These results indicate that, for the ranges tested, sodium chloride concentrations have no effect and may be ignored.

8.0 RELATED WORK

Work has been completed by Peabody and EPA in other areas of flue gas desulfurization chemistry in the presence of high dissolved solids. Specifically:

1. Lime was used instead of limestone.

2. DBA was thoroughly tested as an efficiency enhancement additive.

3. Magnesium was tested as well as more work on sodium cations.

4. Commercial gypsum production through proper cake washing was simulated using a pilot scale belt filter.

The results of these tests will be presented jointly by EPA, Peabody, and Acurex in the forthcoming EPA/EPRI FGD symposium in November. Related research by EPRI and others is tentatively scheduled for the same symposium.

9.0 CONCLUSIONS

The accumulation of dissolved salts in the FGD scrubbing liquor, primarily through the absorption of HCl from the flue gas, had the following effects on the performance of the pilot plant FGD system:

1. A decrease in SO_2 removal efficiency was observed in both the natural and forced oxidation process options. The decrease was shown to be independent of absorber liquid holdup, inlet SO_2 concentration, SO_2 make-per-pass, and liquid to gas ratio. The decrease was not as severe in the forced oxidation mode of operation.

2. Adding excess limestone can restore the SO_2 removal efficiency but the required amount is unacceptably high.

3. Only 650 PPM of the organic acid DBA was required to restore the SO_2 removal efficiency at a chloride concentration of 50,000 mg/l.

4. The decrease in SO_2 removal efficiency in the presence of dissolved solids may easily be predicted using the semi-empirical model developed in this paper.

5. The addition of sodium chloride, instead of calcium chloride, to the pilot plant scrubbing liquor had no effect on SO_2 removal efficiency in the range tested (0 - 25,000 mg/l).

6. Tests run with a base case pH of 6.0 showed a sharper drop in SO_2 removal efficiency than tests run with an initial pH of 5.8. Also, less additional limestone was required to restore the base case removal efficiencies at high calcium chloride concentrations when operating at the lower base case pH.

10.0 ACKNOWLEDGEMENTS

The work performed by Peabody at the Environmental Protection Agency was the first time private industry utilized the government facilities at Research Triangle Park in a joint research effort. The authors made frequent visits to EPA and received extraordinary assistance from all personnel at the Agency. We sincerely wish to thank the following individuals at EPA for making this project possible:

J. David Mobley (Project Officer)
Norman Kaplan
Michael A. Maxwell

In addition, we also wish to thank the following individuals for guidance and technical assistance throughout this program:

Gary T. Rochelle	University of Texas
John C.S. Chang	Acurex Corporation
Herb Dempsey	Acurex Corporation

11.0 REFERENCES

1. Chang, J.C.S., and D. Laslo, "Chloride Ion Effects on Limestone FGD System Performance," Presented at the EPA/EPRI FGD Symposium, May 18, 1982.

2. Hargrove, O.W., et al., "The Effects of Process Water Selection on Lime-Limestone Flue Gas Desulfurization Chemistry," Electric Power Research Institute Report CS-2451, July 1982.

3. Rao, R., and R. Salib, "Designing a Flue Gas Desulfurization System for Worst Case Operating Conditions," Presented at the Air Pollution Control Association Annual Meeting, June 1982.

4. Borgwardt, R.H., "Combined Flue Gas Desulfurization and Water Treatment in Coal Fired Power Plants," Environmental Science & Technology, Vol 14, No. 3, p. 294-298, March 1980.

5. Gleason, R.J., and C.T. Sui, "Process for Drying Calcium Chloride Generated In High Chloride Flue Gas Desulfurization Systems," U.S. Patent No. 4,322,393, March 30, 1982.

6. Becker, D.F., et al., "Effects of Chloride Blowdown on FGD Waste Cnaracteristics," Power Engineering, p.66-68, November 1982.

7. Rader, P.C., R.W. Hanson, and D.C. Borsare, "Design of Lime/Limestone Flue Gas Desulfurization Systems for High Chlorides," Presented at Coal Technology '81, Houston TX, November 1981.

8. Rader, P.C., R.W. Hanson, and D.C. Borsare, "Process Design of Lime/Limestone FGD Systems for High Chlorides," Presented at Coal Technology '82, Houston TX, December 1982.

9. Wang, S.C., and D. Burbank, "Adipic Acid-Enhanced Lime and Limestone Testing at the EPA Alkali Scrubbing Test Facility-Final Report, Volume 1. Basic Report," EPA-600/7-82-010a, NTIS PB 82-230624, March 1982, PP. 198-201.

Table 1
Summary of Test Results - Natural Oxidation

Test ID	NB-1	N2-1	N3-1	N4-1	N5-1	N10-1
Cl- Concentration (mg/l)	167.	20500.	31400.	40530.	50100.	101600.
L/G (liters/cu. m.)	8.0	8.0	8.0	8.0	8.0	8.0
Absorber Feed pH	6.0	5.3	5.2	5.1	4.9	4.6
Absorber Effluent pH	5.6	4.9	4.9	4.6	4.5	4.0
SO_2 Inlet Conc. (PPM)	2565.	2565.	2565.	2611.	2565.	2513.
SO_2 Removal Efficiency (%)	79.	73.	70.	62.	58.	33.
SO_2 Make-per-pass (mM)	8.4	7.8	7.5	6.7	6.2	3.4
Limestone Utilization	80.	76.	75.	72.	72.	75.
Filter Cake Solids Conc. (wt%)	53.0	47.0	49.0	52.0	52.3	50.9
Solids Settling Rate (cm/min)	0.5	0.3	0.3	0.3	0.2	0.2
Gypsum Saturation Feed (%)	50.2	89.9	94.1	116.9	115.6	96.0
Gypsum Saturation Effluent (%)	67.7	131.8	134.9	171.0	139.5	137.6
Height Packing (cm)	53.3	53.3	53.3	53.3	53.3	53.3
R (from Eq. (6))	1.0	0.91	0.77	0.61	0.56	0.25

Table 2

Summary of Test Results - Forced Oxidation

Test ID	FB-3	F2-1	F5-1	F8-1	F18-1
Cl- Concentration (mg/l)	0.	20000.	50200.	80130.	179700.
L/G (liters/cu. m.)	8.0	8.0	8.0	8.0	8.0
Absorber Feed pH	5.9	5.8	5.7	5.5	5.2
Absorber Effluent pH	5.1	4.9	4.6	4.4	4.1
SO_2 Inlet Conc. (PPM)	2470.	2330.	2456.	2483.	2502.
SO_2 Removal Efficiency (%)	80.	79.	73.	66.	35.
SO_2 Make-per-pass (mM)	8.4	8.1	7.7	7.0	3.7
Limestone Utilization	86.	85.	82.	80.	61.
Filter Cake Solids Conc. (wt%)	78.2	78.6	77.2	78.5	79.4
Solids Settling Rate (cm/min)	4.9	4.5	4.2	4.3	0.9
Gypsum Saturation Feed (%)	N/A	N/A	139.7	128.8	N/A
Gypsum Saturation Effluent (%)	N/A	N/A	208.0	157.1	N/A
Height Packing (cm)	53.3	53.3	53.3	53.3	53.3
R (from Eq. (6))	1.0	0.95	0.80	0.67	0.26

N/A = Data not available or not applicable

Table 3
Summary of Test Results - Low Make-Per-Pass Runs

Test ID	NB-10	NB-11	N5-LM1	N5-LM2	N5-LM3	N5-LM4
Cl- Concentration (mg/l)	0.	0.	50000.	50000.	50000.	50000.
L/G (liters/cu. m.)	10.7	4.5	10.7	10.7	4.7	4.7
Absorber Feed pH	5.8	5.9	4.9	5.2	5.4	5.8
Absorber Effluent pH	5.4	5.5	4.4	4.7	5.1	5.6
SO_2 Inlet Conc. (PPM)	2496.	493.	2513.	2492.	515.	508.
SO_2 Removal Efficiency (%)	56.	52.	47.	57.	43.	55.
SO_2 Make-per-pass (mM)	4.5	1.9	3.9	4.7	1.5	2.0
Limestone Utilization	84.	82.	90.	52.	80.	48.
Filter Cake Solids Conc. (w%)	60.8	N/A	69.4	N/A	68.7	N/A
Solids Settling Rate (cm/min)	0.6	0.6	0.6	N/A	0.5	N/A
Gypsum Saturation Feed (%)	88.7	N/A	131.5	N/A	137.3	N/A
Gypsum Saturation Effluent (%)	100.8	N/A	195.8	N/A	157.2	N/A
Height Packing (cm)	0.0	0.0	0.0	0.0	0.0	0.0
R (from Eq. (6))	1.0	1.0	0.77	N/A	0.77	N/A

N/A = Data not available or not applicable

Table 4
Summary of Test Results - High Make-Per-Pass Runs

Test ID	NB-8	NB-9	N5-HM1	N5-HM2	N5-HM3	N5-HM4
Cl- Concentration (mg/l)	0.	0.	50000.	50000.	50000.	50000.
L/G (liters/cu. m.)	11.2	7.2	11.2	11.2	7.2	7.2
Absorber Feed pH	5.8	5.9	5.0	5.2	5.1	5.4
Absorber Effluent pH	5.5	5.5	4.5	4.7	4.7	5.2
SO_2 Inlet Conc. (PPM)	2448.	483.	2517.	2507.	512.	510.
SO_2 Removal Efficiency (%)	89.	92.	81.	90.	84.	91.
SO_2 Make-per-pass (mM)	7.7	2.3	6.7	7.4	2.1	2.2
Limestone Utilization	85.	88.	86.	63.	83.	43.
Filter Cake Solids Conc. (w%)	61.6	N/A	59.3	N/A	83.7	N/A
Solids Settling Rate (cm/min)	0.6	0.6	0.5	N/A	0.5	N/A
Gypsum Saturation Feed (%)	N/A	58.8	132.8	N/A	125.8	N/A
Gypsum Saturation Effluent (%)	N/A	63.5	202.7	N/A	155.5	N/A
Height Packing (cm)	64.8	64.8	64.8	64.8	64.8	64.8
R (from Eq. (6))	1.0	1.0	0.75	N/A	0.73	N/A

N/A = Data not available or not applicable

Table 5
Summary of Test Results - Sodium Testing

Test ID	NB-1	NN-1	NN-2
Cl- Concentration (mg/l)	167.	25000.	50000.
L/G (liters/cu. m.)	8.0	8.0	8.0
Absorber Feed pH	6.0	5.9	5.2
Absorber Effluent pH	5.6	5.5	4.8
SO_2 Inlet Conc. (PPM)	2565.	2503.	2514.
SO_2 Removal Efficiency (%)	79.	79.	72.
SO_2 Make-per-pass (mM)	8.4	8.4	7.6
Limestone Utilization	80.	72.	70.
Filter Cake Solids Conc. (w%)	53.0	57.0	59.0
Solids Settling Rate (cm/min)	0.5	N/A	N/A
Gypsum Saturation Feed (%)	50.2	27.4	124.1
Gypsum Saturation Effluent (%)	67.7	30.5	169.4
Height Packing (cm)	53.3	53.3	53.3
Sodium Conc. (mg/l)	73.	16300.	16650.
Calcium Conc. (mg/l)	385.	932.	13850.
R (from Eq. (6))	1.0	1.0	0.81

N/A = Data not available or not applicable

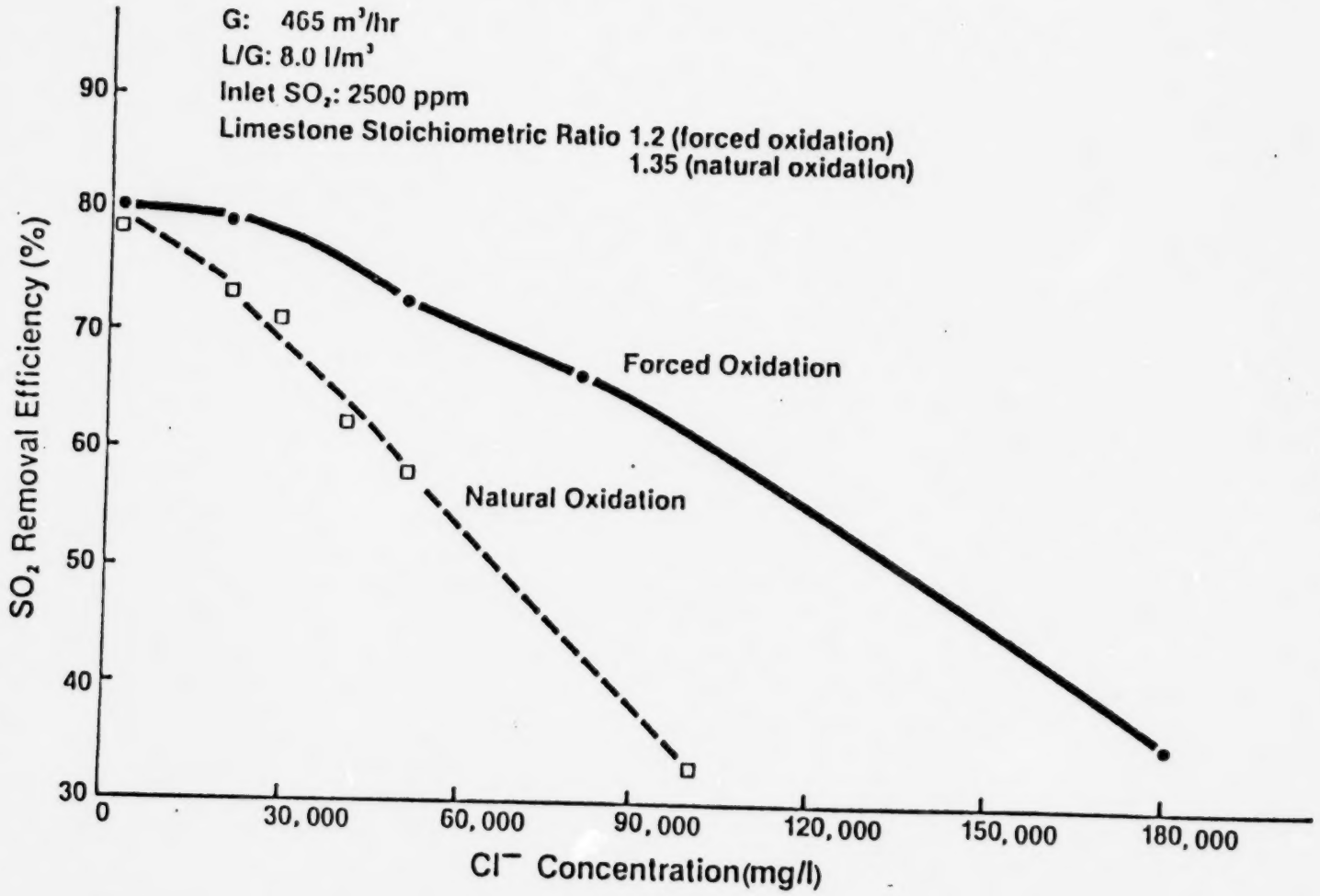

Figure 1. Comparison of natural and forced oxidation SO_2 removal efficiencies as a function of slurry chloride concentration.

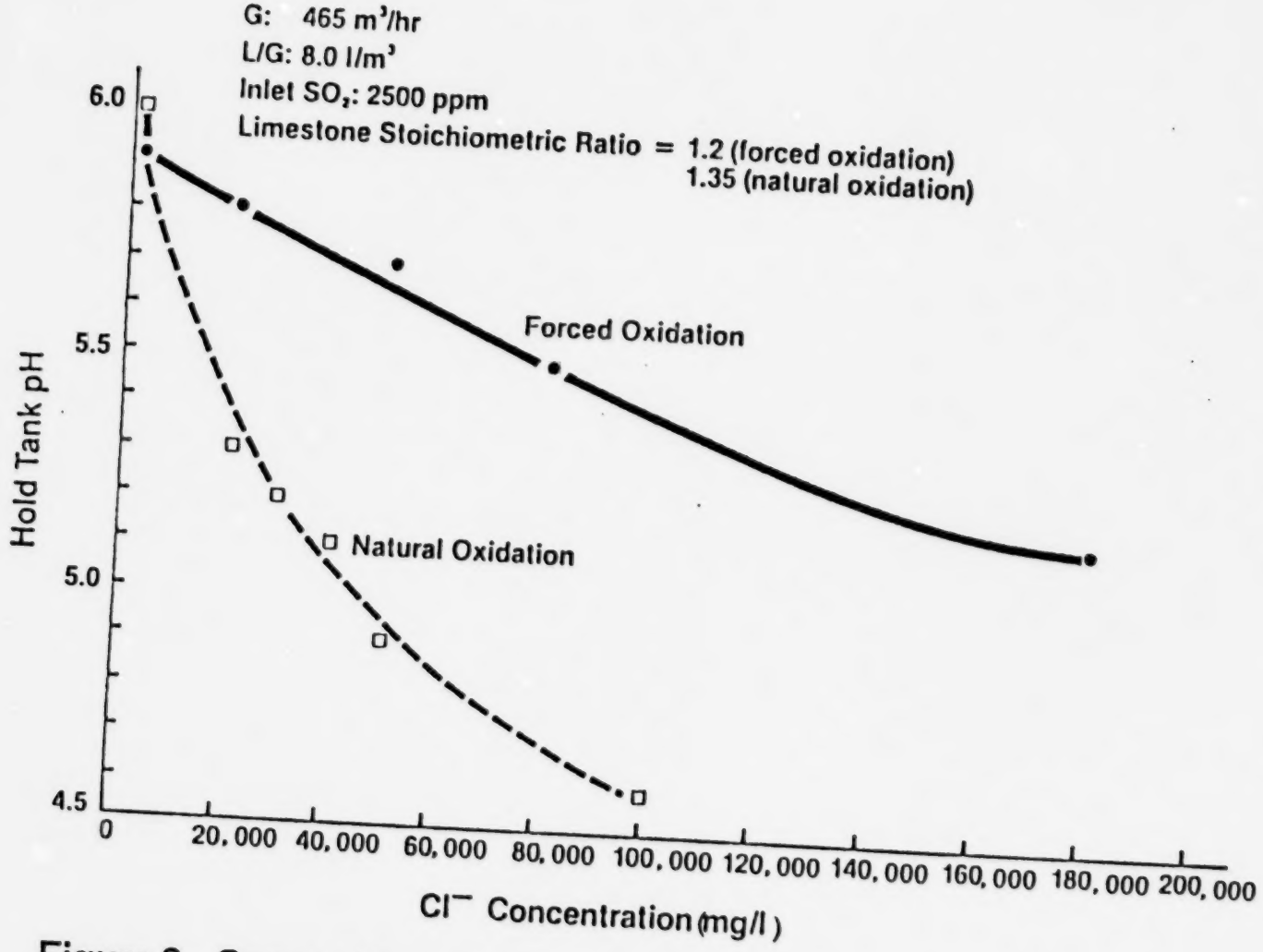

Figure 2. Comparison of natural and forced oxidation hold tank pH's.

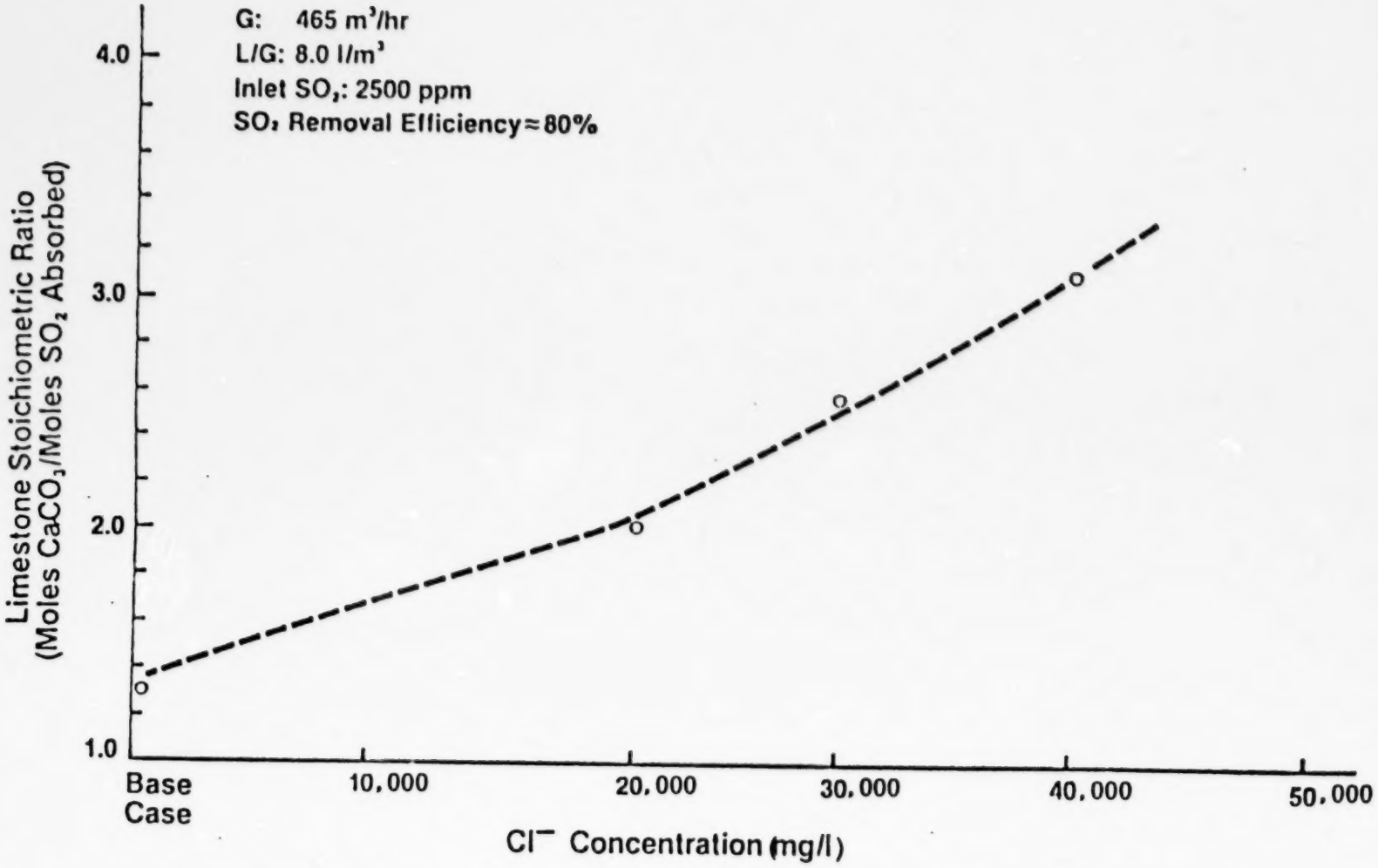

Figure 3. Limestone stoichiometric ratio required for 80% SO_2 removal vs. Cl^- concentration with natural oxidation.

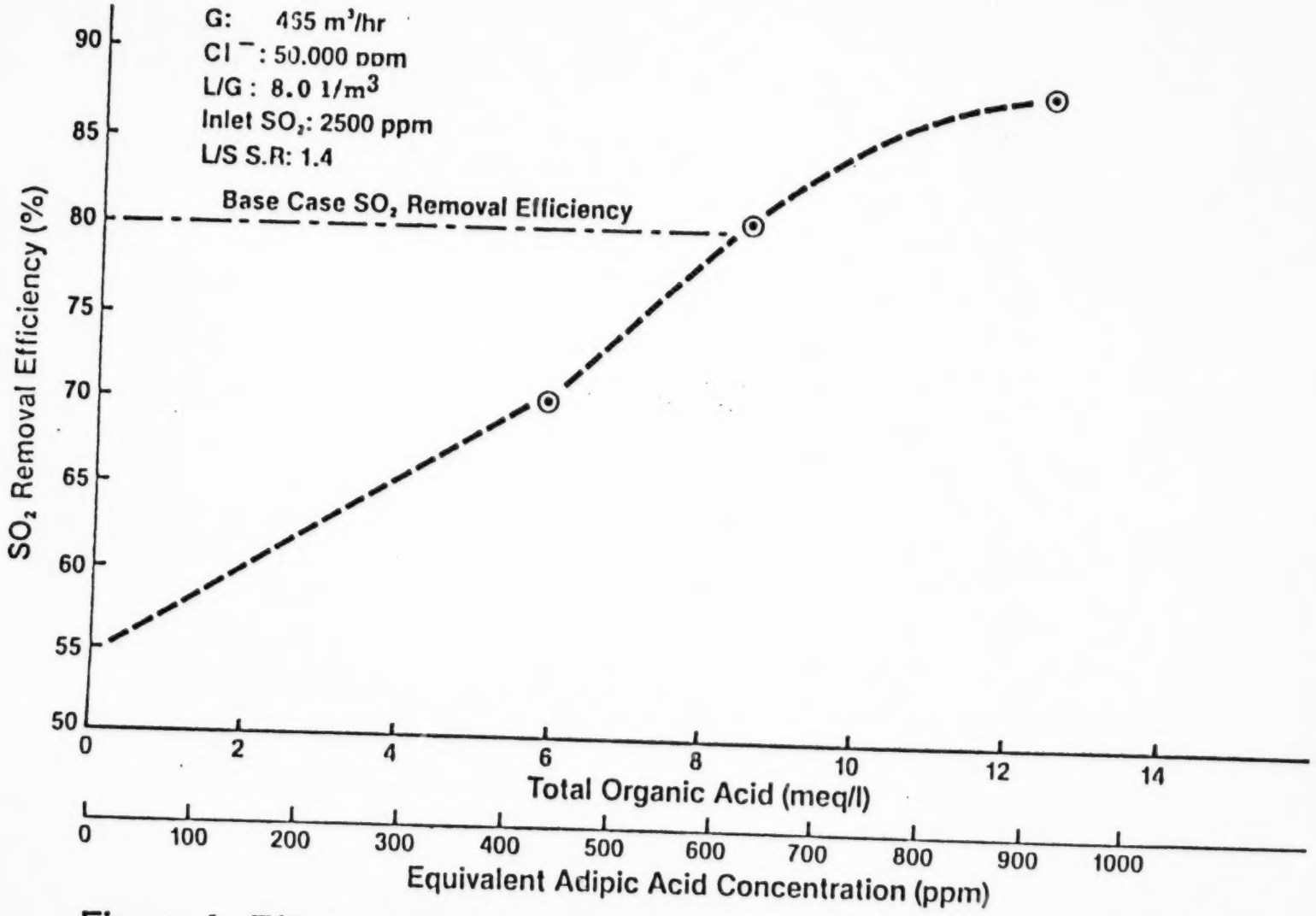

Figure 4. Effect of organic acid concentration on SO_2 removal efficiency at 50,000 ppm chloride with natural oxidation.

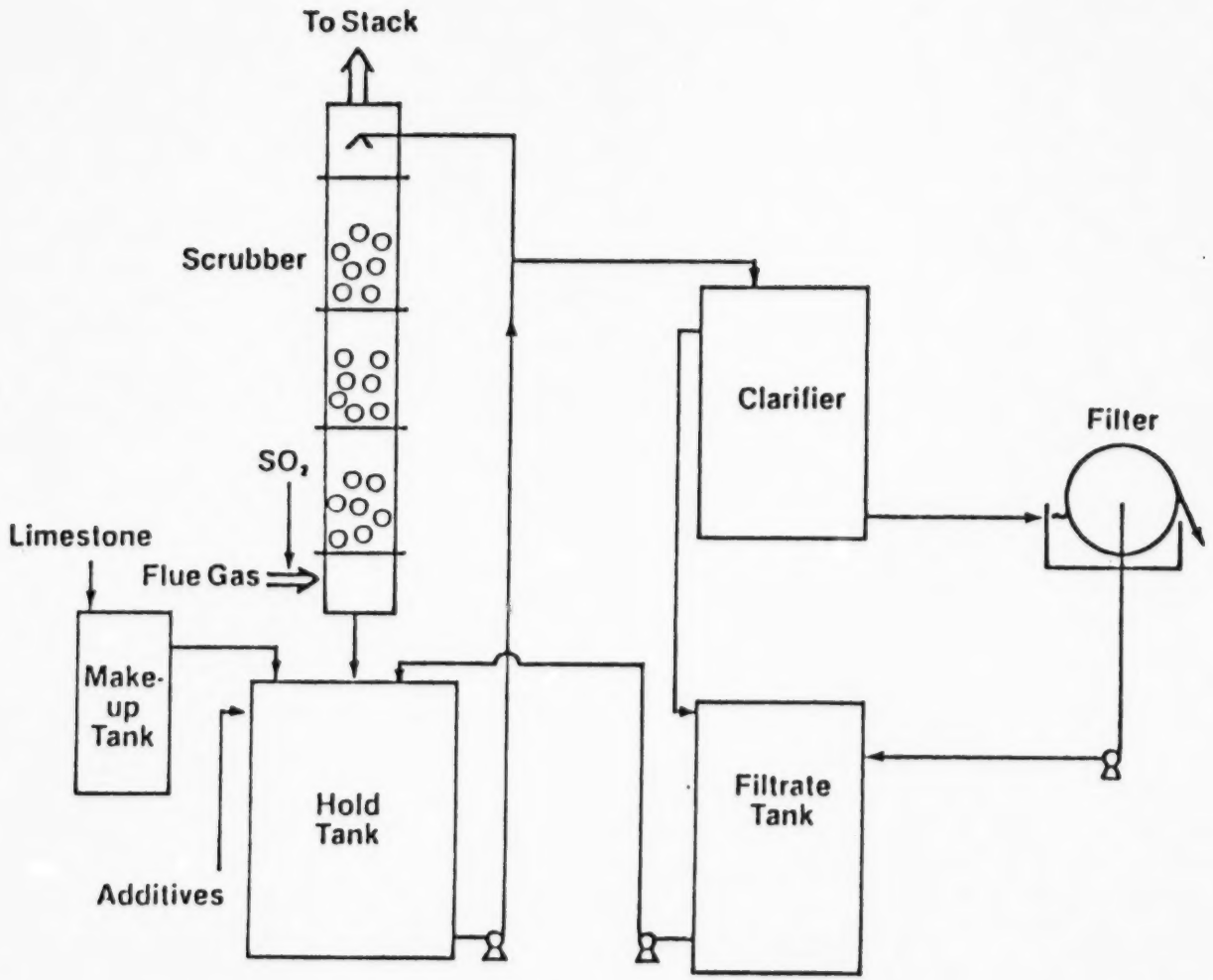

Figure 5. Flow diagram for single-loop natural oxidation tests in the 0.1 MW limestone pilot plant system.

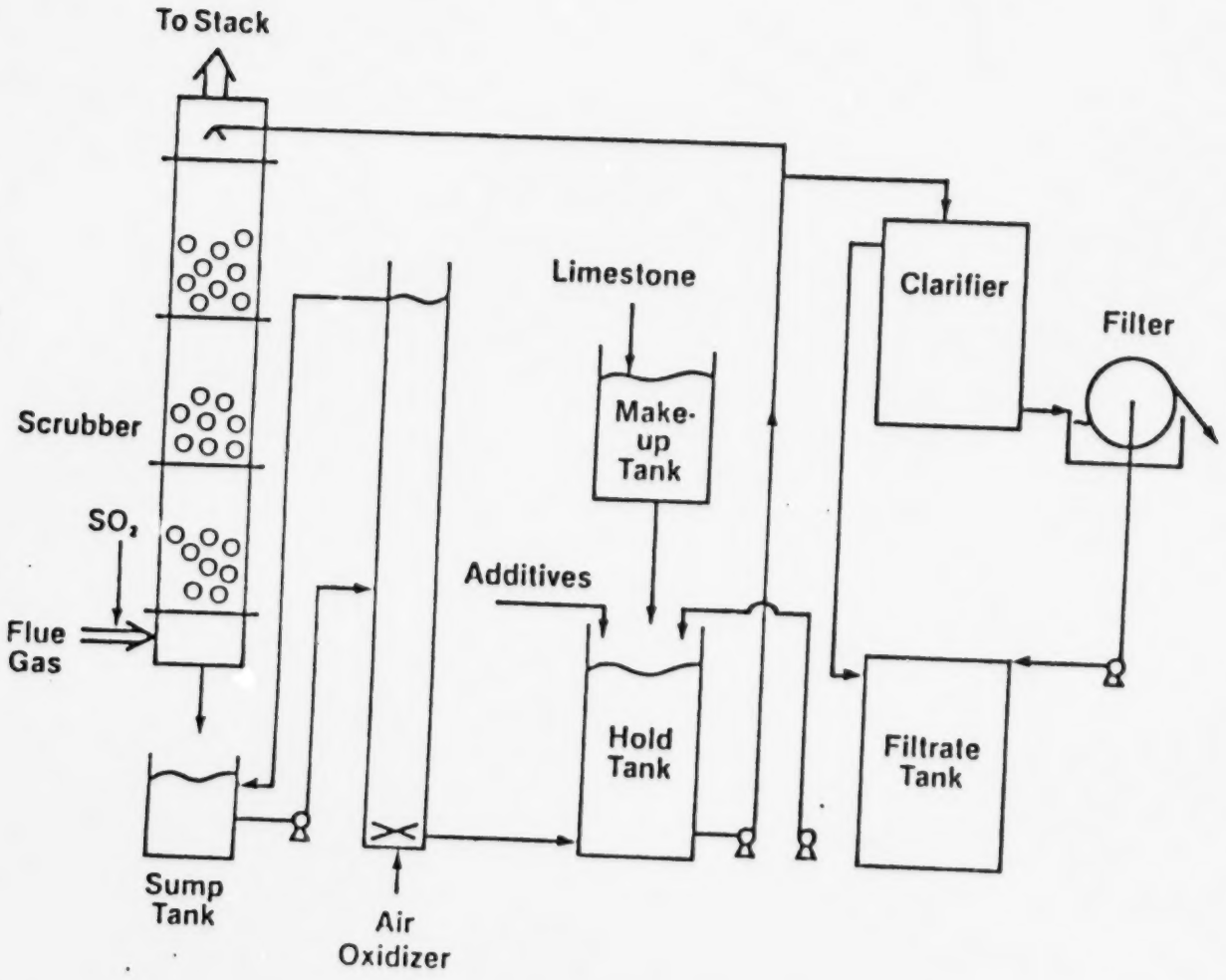

Figure 6. Flow diagram for the in-loop forced oxidation tests in the 0.1 MW limestone pilot plant system.

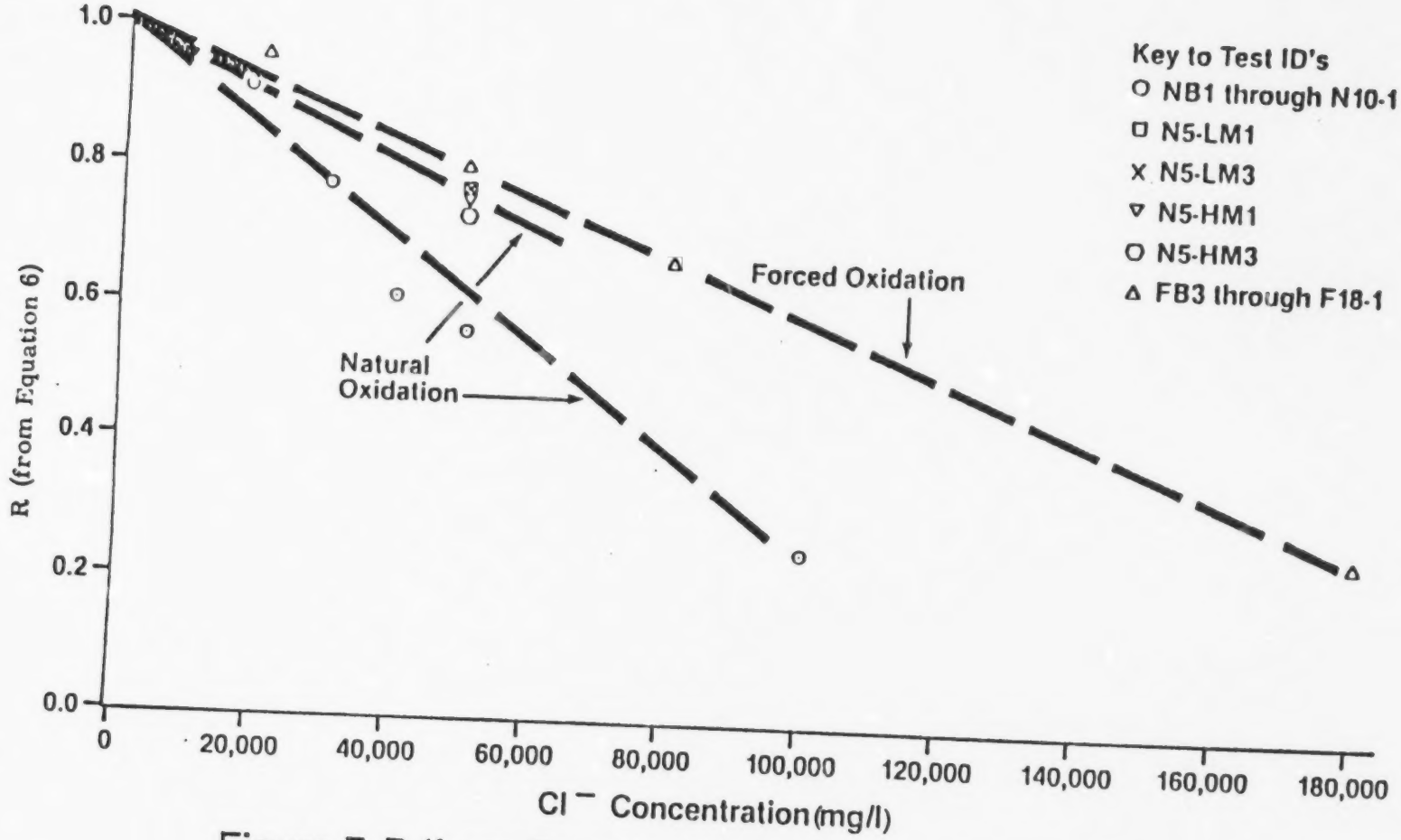

Figure 7. R (from Equation 6) vs chloride concentration.